ESTIMATION OF PHENOLS IN WATER BY MEANS OF ULTRAVIOLET ABSORPTION SPECTRA

BY
EDWARD CLARENCE DUNLOP
A.B., Westminster College, 1936
M.S., University of Illinois, 1938

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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ACKNOWLEDGMENTS

The author wishes to express his appreciation to Professor A. M. Buswell for his supervision of this investigation and also to thank members of the State Water Survey staff for many helpful discussions.

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Introduction

The problem of the estimation of phenols in water is of interest because of the serious objectionable tastes and odors they cause in water supplies upon chlorination. A number of procedures have been devised for the determination of phenols and at the present time the bromide-bromate titration method as applied by Scott[1] is considered the best method for solutions containing not less than 50 mg. phenol per liter. Colorimetric methods[2] are available for lower concentrations but their application is questionable.

Recently apparatus for the determination of the absorption spectra of substances in the ultraviolet region has been developed to the point where the time consumed in obtaining the absorption spectrum is relatively short. This technique has been applied to the analysis of small amounts of material in solution.[3] The present investigation shows the application of absorption spectra determinations to the analysis of phenols in water. Studies were also made on the relation of ultraviolet absorption spectra to biochemical oxygen demand and to odors.

Experimental

The absorption spectra data were determined with a Bausch and Lomb Medium Quartz Spectrograph and Sector Photometer. The light source was a condensed spark with tool-steel electrodes which gave a large number of lines uniformly distributed over the entire spectrum range used. Eastman D. C. Ortho plates were used and the absorption cells were fused quartz and were matched in length and absorbing properties. The length was accurately known to the nearest 0.0001 cm.

The experimental procedure consisted of determining the molecular extinction coefficient under definite conditions and

then applying the same procedure to the determination of the concentrations of unknown solutions.

The theoretical basis for such a procedure is that the solutions obey both the Bouguer-Lambert and Beer laws for the concentration range used. This was found to be true for all the solutions studied.

The fundamental equation, which is formed by the combination of the two laws, $\log I_0/I = E = \epsilon cl$, where I_0 is the incident light, I the transmitted light, E the extinction or density, ϵ the molecular extinction coefficient, c the molar concentration and l the length of absorbing solution, is used for calculating the results from the measured extinction value, E.

Results and Discussion

The molecular extinction coefficient of phenol in water solution has been determined for concentrations of 0.0010 to 0.0104 grams per liter in cell lengths of 10.018 and 1.994 cm. The molecular extinction coefficient is found to be constant with 1496 as the average value, with the position of the maximum absorption being at a wave length of 2693 Å. Attempts to increase the sensitivity of the test by increasing the molecular extinction coefficient by the addition of sodium hydroxide, by extraction of the phenol into a solvent in which it would have a higher molecular extinction coefficient, or by the formation of chloro derivatives were not successful.

A series of solutions containing unknown amounts of phenol were analyzed by measuring the extinction value at 2693 Å and calculating the concentration from the above equation. The data in the following table (Table I) show that accurate results are obtained and that the procedure is good down to a few parts per million.

TABLE I

ANALYSIS OF SOLUTIONS FOR PHENOL

Unknown Sample	Phenol found mg./1.	Phenol "actual" mg./1.	Error	% Error
1	3.25	3.31	0.06	1.8
2	3.22	3.31	0.09	2.7
3	4.84	4.73	0.11	2.3
4	18.9	20.0	1.1	5.5
5	38.8	40.0	1.2	3.0

The molecular extinction coefficient of *o*-cresol in water solution has been determined for concentrations of 0.00098 to 0.01019 grams per liter in cell lengths of 10.018 and 1.994 cm. The maximum molecular extinction coefficient is found to be 1668 at a wave length of 2719 Å. For *m*-cresol in water solutions of concentrations of 0.00102 to 0.01027 grams per liter in cell lengths of 10.018 and 1.994 cm. the maximum molecular extinction coefficient is found to be 1544 at a wave length of 2717 Å. For *p*-cresol in water solutions of concentrations of 0.00104 to 0.01040 grams per liter in cell lengths of 10.018 and 1.994 cm. the maximum molecular extinction coefficient is found to be 1656 at a wave length of 2773 Å.

An equal mixture of the three cresols is found to give a maximum extinction coefficient of 1636 at a wave length of 2740 Å. This is what would be expected from an average of the three individual values. It is found that mixtures of phenol and cresols give molecular extinction values which are between their individual values. This is the basis for the use of the average molecular extinction coefficient value and the average molecular weight in the equation in calculating the concentration of phenols in solutions containing mixtures of phenol and cresols. The equation is $E = 1556 \times \frac{c}{101} \times l$, and it has been applied to the following series of unknowns with good results as is shown in the following table (Table II).

TABLE II

ANALYSIS OF SOLUTIONS FOR PHENOLS

Unknown Sample	Phenols found mg./1.	Phenols "actual" mg./1.	Error	% Error
1	2.00	2.02	0.02	1.0
2	3.35	3.50	0.15	4.2
3	5.93	6.02	0.09	1.4
4	15.2	16.0	0.8	5.0
5	15.8	16.0	0.2	1.2
6	5.02	5.04	0.02	0.4

It may be summed up then that phenolic solutions containing down to approximately one part per million can be analyzed by the spectroscopic method with an error of between 0 and 5 per cent using cells up to ten centimeters in length.

From the studies on the relation of ultraviolet absorption spectra to biochemical oxygen demand it was found that no quantitative relation existed. It was also concluded that studies in the short wave length ultraviolet would possibly give better results.

From the spectroscopic data on several odorous compounds and an extensive review of the literature[4,5,6] no correlation was found between ultraviolet absorption spectra and odor. In the course of this study the absorption spectra of some compounds were determined which have not appeared in the literature and therefore their absorption curves have been given. The data are shown in the following table (Table III).

TABLE III

Borneol in alcohol	λmax. $<$2300 Å	ϵ2300 = 3.1
Borneol in hexane	λmax. $<$2300 Å	ϵ2300 = 2.5
Isoborneol in alcohol	λmax. $<$2300 Å	ϵ2300 = 0.45
Isoborneol in hexane	λmax. $<$2300 Å	ϵ2300 = 0.40
Terpinolene in alcohol	λmax. $<$2300 Å	ϵmax. $>$ 1800
Terpinolene in hexane	λmax. $<$2300 Å	ϵmax. $>$ 1800
d α-Phellandrene in alcohol	λmax. = 2610±5 Å	ϵmax. = 1125
d α-Phellandrene in hexane	λmax. = 2610±5 Å	ϵmax. = 1010
Dipentene in alcohol	λmax. = 2660±5 Å	ϵmax. = 210
Dipentene in hexane	λmax. = 2660±5 Å	ϵmax. = 200

The infrared absorption spectra of borneol and isoborneol in carbon tetrachloride give peaks at 2.75 μ, 2.85-2.93 μ and 3.37 μ which are assigned to free OH, bonded OH and CH frequencies respectively. The molecules are highly associated as the bonded peak increases strongly on increased concentration.

BIBLIOGRAPHY

1. Scott, R. D., Ind. Eng. Chem. An. Ed. **3**, 67 (1931).
2. Standard Methods for the Examination of Water and Sewage, American Public Health Association, New York, 8th Ed., (1936).
3. Twyman, F. and Allsopp, C. B., The Practice of Absorption Spectrophotometry with Hilger Instruments, Adam Hilger, LTD. London, (1934), p. 26.
4. Fairbrother, T. H., Ind. Chem. **2**, 385 (1926).
5. Dyson, G. M., Perfumery Ess. Oil Record. **28**, 13 (1937).
6. International Critical Tables, Vol. 5 (1929), p. 359.

VITA

The author was born January 18, 1916 in Center, Missouri. He received his elementary and secondary education at Center, Missouri, graduating from High School in 1932. He attended Hannibal La Grange College during 1932-1933 and Westminster College from 1933 to 1936 where he received the A. B. degree in June 1936. He entered the University of Illinois Graduate School in the summer of 1936 leaving in the fall to be an instructor in chemistry at Westminster College. He returned to the University of Illinois in the summer of 1937 and received the M. S. degree in 1938. He has been a research assistant for the Illinois State Water Survey from October, 1940 until February, 1942. He is a member of Sigma Xi. He is the co-author of the following publications.

Buswell, A. M., Dunlop, E. C., Rodebush, W. H., and Swartz, J. B., "Change of the Ultraviolet Absorption Spectrum of Acrolein with Time," J. Am. Chem. Soc. *62* 325, 1940.

Dunlop, E. C., Williamson, B., Rodebush, W. H., and Buswell, A.M.; "Ultraviolet Absorption of Diphenic Acids," J. Am. Chem. Soc. *63* 1167, 1941.